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# Indian Standard CODE OF SAFETY FOR NITROBENZENE

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INDIAN STANDARDS INSTITUTION
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NEW DELHI 110002



### Indian Standard CODE OF SAFETY FOR NITROBENZENE

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# Indian Standard CODE OF SAFETY FOR NITROBENZENE

#### 0. FOREWORD

- **0.1** This Indian Standard was adopted by the Indian Standards Institution on 18 February 1977, after the draft finalized by the Chemical Hazards Sectional Committee had been approved by the Chemical Division Council.
- 0.2 Nitrobenzene is a pale yellow liquid with a distinct almond like odour. The colour of the liquid varies from pale yellow to yellowish brown depending on the purity of the compound. Being a high boiling paint liquid, the probability of poisoning by inhalation of vapour from the cold liquid is not much. Since nitrobenzene is a highly toxic substance, it will produce either acute poisoning by absorption of a large amount in a short time or chronic poisoning by continued exposure to small amounts. It can be absorbed by inhalation, ingestion or directly through the intact skin. Its toxic reaction is enhanced by subsequent ingestion of ethanol. In industry the major hazard is absorption through the skin. Observance of this code of safety will reduce the frequency and severity of hazard.
- 0.2.1 Nitrobenzene is also known as oil of mirbane or nitrobenzol and is represented by the formula, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>.
- **0.3** The reduction of nitrobenzene to aniline probably outranks all other uses of nitrobenzene as an industrial chemical and reflects the importance of it as the starting material for dyestuffs and other organic intermediates.
- **0.4** The properties of nitrobenzene listed under 3 have been taken from literature and have been included for information only. Moreover, these properties pertain to pure nitrobenzene. For technical nitrobenzene IS: 2630-1973\* has been published.
- 0.5 In the preparation of this code, assistance has been derived from Chemical Safety Data Sheet No. 21 'Nitrobenzene' issued by the Manufacturing Chemists' Association, USA.

<sup>\*</sup>Specification for nitrobenzene (first revision).

#### 1. SCOPE

- 1.1 This standard describes properties of nitrobenzene, the nature of hazards associated with it and essential information on its storage, handling, packing, labelling, disposal of waste, cleaning and repairing of containers, selection and training of personnel protective equipment and first aid.
- 1.1.1 This code does not deal with specification for design of buildings, chemical engineering plants, storage vessels, equipment for operations control and waste disposal.

#### 2. TERMINOLOGY

2.1 For the purpose of this standard, the definitions given in IS: 4155-1966\* shall apply.

#### 3. PROPERTIES OF NITROBENZENE

- 3.1 The important properties of nitrobenze are:
  - a) Appearance Light to dark yellow liquid.
  - b) Odour Sweet and characteristic, bitter-almond like.
  - c) Relative Density at 20°C/4°C (water = 1) = 1.204.
  - d) Vapour Density (air = 1) = 4.24.
  - e) Boiling Point (at 760 mm) 210 to 212°C.
  - f) Freezing Point 4.97 to 5.13°C.
  - g) Flash Point Closed Cup 87.8°C Open Cup 77°C.
  - h) Explosive Limit Lower, 1.8 percent by volume in air at 93.3°C.
  - j) Corrosiveness None.
  - k) Solubility 0.19 percent soluble in water at 15.6°C.
  - l) Spontaneous Ignition Temperature 495.6°C.
  - m) Oxidation Oxidizing agent.

#### 4. HAZARDS ASSOCIATED WITH NITROBENZENE

**4.1 Health Hazards** — Nitrobenzene is highly toxic when absorbed through the skin, inhaled as vapour, or swallowed. Although toxic, nitrobenzene may be handled safely if power precautions are constantly observed.

<sup>\*</sup>Glossary of terms relating to chemical and radiation hazards and hazardous chemicals.

4.1.1 Nitrobenzene is readily absorbed by direct contact through the intact skin, by inhalation of the vapour, or when ingested. Absorption in toxic quantities first manifests itself by cyanosis or 'blue lip'. A bluish tinge may be seen in the finger nailbeds, lips, lobes of ears, conjunctiva, mucous membranes, and tongue. Cyanosis is caused by the conversions of the homoglobin of the red blood cells to methemoglobin, which, unlike hemoglobin or oxyhomoglobin, is incapable of releasing its oxygen content to the tissues of the body so that varying degrees of tissue anoxis or asphyxia result. Early in this type of poisoning, a mild euphoria or sense of well being is usually noted. As the concentration of methemoglobin rises, a patient complains of headache, drowsiness and occasionally of nausea and vomiting. If the methemoglobin content continues to rise, the patient becomes stuporous, and he may even become unconscious. Such patients are seriously ill and death may ensue, if proper treatment is not promptly rendered.

#### 4.1.2 Acute Toxicity

- **4.1.2.1** Toxic effects The toxic effects of nitrobenzene are essentially acute and give the signs and symptoms described in **4.1.1**.
- **4.1.2.2** Local effects Very rarely a dry scaly dermatitis may develop in workers exposed to nitrobenzene and is probably due to the defatting action of nitrobenzene upon the skin.

#### 4.1.3 Chronic Toxicity

- 4.1.3.1 Systemic effects Repeated exposures to low concentrations of nitrobenzene may give rise to a clinical picture which has been reported as chronic nitrobenzene poisoning. Such cases may present varying degrees of pallor, low-grade secondary anaemia, fatigability and anorexia. However, upon complete cessation of exposure, such individuals promptly regain their normal levels of health with no permanent residual pathology being demonstrable.
- 4.1.3.2 Nitrobenzene tumors of the bladder It has been thoroughly demonstrated that the absorption of nitrobenzene never gives rise to tumors of the bladder, either benign or malignant. The term 'Nitrobenzene Tumors' is, therefore, a misnomer.
- **4.1.4** Threshold Limit Value (TLV\*) in Air The upper limit of nitrobenzene vapour concentration considered safe for continuous exposure for 8 hours work day and 40 hours work week is 1 ppm.

<sup>\*</sup>As accepted by American Conference of Governmental Industrial Hygienists, USA.

#### 4.2 Fire and Explosion Hazards

4.2.1 Fire Hazard — Nitrobenzene is combustible. Although the vapour given off at elevated temperatures is flammable, nitrobenzene may be handled with little danger of fire. The flash point of the liquid is much higher than the temperatures at which it is normally handled. Flammable toxic vapour may be given off at elevated temperatures if the material becomes involved in the fire.

#### 4.2.2 Fire Fighting

- **4.2.2.1** Although nitrobenzene is a nitrated compound, it behaves much like a straight hydrocarbon, that is, it requires an external supply of oxygen to burn.
- **4.2.2.2** Use carbon dioxide, dry chemical or foam extinguishers when fire is still small.
- 4.2.2.3 In case the fire gains headway, it becomes difficult to approach the fire because of too fierce flames and toxic gas. Put on breathing apparatus while fighting fire.
- 4.2.2.4 Water may be used successfully if applied in the form of a fog or spray. It is advisable to enclose the fire area with water jets.
- 4.2.3 Explosion Hazard Nitrobenzene is not likely to explode, as are the higher nitrated derivatives. However, when this is heated beyond its flash point it becomes as dangerous as gasoline at normal temperature. Such mass of air which contain more than 1.8 percent of the vapour can be exploded at a temperature greater than the flash point.
- 4.2.3.1 Nitrobenzene should never come in contact with strong alkalis, like caustic soda and caustic potash, as a violent reaction ensues, and the mixture may catch fire giving rise to moxious fumes. Also, during manufacture of nitrobenzene, the concentration of m-dinitrobenzene remains below 0.01 percent.

#### 5. ENGINEERING CONTROLS

5.1 Equipment Design — The operation should be carried out in a perfectly closed type system. Because of the toxic nature of the material, equipment to handle nitrobenzene should be located in the open area or well ventilated area.

#### 5.2 Ventilation

5.2.1 Good natural ventilation is considered sufficient in places where nitrobenzene is handled. Since nitrobenzene vapour is 4.24 times heavier than air, a down draught mechanical exhaust may be needed in those operations where general ventilation is considered inadequate. The air flow should be away from the work area.

- 5.2.2 Vent lines from closed system holding vessels should be extended well above the roof level of process buildings, so that vapour shall not enter buildings.
- 5.3 Air Monitoring Certain regulations prescribe testing of atmosphere where the processes of manufacturing or manipulation of nitrocompounds are being carried out. Routine monitoring of contamination level indicates effective functioning of technical control measures and steps to be taken if it is not so.

#### 6. STORAGE AND HANDLING

#### 6.1 Storage

- 6.1.1 Location of Storage Tanks Nitrobenezene is commonly stored in a steel tank. Locate storage tanks away from any area where fire hazard is acute. Bulk storage tanks should be located in the open.
  - 6.1.2 Caution to be Observed During Storage
- 6.1.2.1 Provide each tank with a vent protected by a flame arrestor and terminating outdoor.
- **6.1.2.2** Earth every tank to prevent static electricity from accumulating.
- 6.1.2.3 Build a dyke around storage tanks to keep the liquid from flowing out, so that disposal can be controlled in case the tank is ruptured.
- 6.1.2.4 Inspect every tank periodically, and keep it under safe conditions.

#### 6.2 Caution to be Taken During Transportation

- 6.2.1 When nitrobenzene is transported, refrain from transporting it together with other materials.
- 6.2.2 Adequate care shall be taken not to drop the containers or cause them any damage.
- 6.2.3 Put a sign in a conspicuous place indicating the presence of hazardous chemical.
  - 6.2.4 Protect the containers from direct sunlight.
  - 6.2.5 No smoking should be permitted in the vicinity of the material.

#### 6.3 Caution to be Taken During Use

6.3.1 Since drums are not pressure containers, do not use any pressurized gas to transfer nitrobenzene from the drums.

- 6.3.2 Avoid direct contact with skin.
- 6.3.3 Persons handling it shall wear personal protective equipment, such as, goggles, aprons, gloves, and rubber sheets.
- 6.3.4 Workers should be instructed emphasizing the need for handling nitrobenzene in accordance with approved method.
- 6.3.5 For emptying drums, place the bung up and use a bung wrench to remove the body plug. Stand on the side and open the plug about half turn. Allow the internal pressure, if any, to release and then open it full.
  - **6.3.6** Do not use empty containers for any other product.
- 6.3.7 The empty containers, before discarding, should be thoroughly cleaned of their contents and treated with an inactivating agent.

#### 7. PACKING AND LABELLING

#### 7.1 Packing

- 7.1.1 The material shall be packed in suitable drums conforming to IS: 2552-1970\*.
- 7.1.2 Each container shall be securely closed and shall bear legibly and indelibly the following information:
  - a) Name of the material;
  - b) Name of the manufacturer;
  - c) Lot/batch number;
  - d) Net, gross and tare mass; and
  - e) Poison label [Figure 5 of IS: 1260 (Part I)-1973†].
- 7.1.3 In addition, the following cautionary notice shall also be displayed on each container:

DANGER! KEEP WELL CLOSED AND PROTECTED FROM DIRECT SUNLIGHT. NITROBENZENE IS ABSORBED THROUGH THE SKIN. AVOID CONTACT WITH SKIN.

#### 7.2 Labelling

- 7.2.1 Each container (including tank car) should have an identifying label.
- 7.2.2 Every vehicle carrying one or more containers of nitrobenzene shall bear 'DANGEROUS' placards.

<sup>\*</sup>Specification for steel drums (galvanized and ungalvanized) (first revision). †Pictorial markings for handling and labelling of goods: Part I Dangerous goods ( first revision ).

7.2.3 The following cautionary label is recommended for use in combination with any other statements required by statutes, regulations, etc:

#### NITROBENZENE

DANGER. EXTREMELY HAZARDOUS. LIQUID AND VAPOUR RAPIDLY ABSORBED THROUGH THE SKIN. SHOULD NOT GET IN EYES, ON SKIN, ON CLOTHING. AVOID BREATHING VAPOUR. USE ONLY WITH SUFFICIENT VENTILATION.

7.2.3.1 In case of contact, remove at once contaminated clothing including footwear and flush skin or eyes with plenty of water (preferably tepid warm) for at least 15 minutes. Get medical aid. Launder clothing before re-use.

#### 8. TANK AND EQUIPMENT CLEANING AND REPAIRS

#### 8.1 Preparation of Tank and Equipment

- 8.1.1 Since inspection, washing and repairs of tanks are hazardous operations, cleaning should be done under the direct supervision of trained personnel who are thoroughly familiar with the hazards and the safeguards necessary for the safe performance of the work. The main hazards are exposure to nitrobenzene (liquid and vapour).
- 8.1.2 Tanks and equipments pumps, lines and valves should be drained and washed before being repaired. No attempt should be made to repair equipments till free of nitrobenzene. While opening flanges, the lower bolts farthest away should be loosened first, taking care to avoid contact with the drippings.
- 8.1.3 Pipelines into or out of the tank should be disconnected, preferably by removing a complete small section and providing a blank flange on the open end to protect against human error and unsuspected leaks. Valves, cocks should not alone be relied upon.
- 8.1.4 Remove completely the residues by washing the tank with cool water. Then wash the tank with hot water (60°C) repeatedly.
- 8.1.5 Introduce live steam in the tank, keeping open the bottom outlet for constant drainage of condensate water.
- **8.1.6** When all nitrobenzene smell is gone, cool the tank, and confirm the absence of nitrobenzene liquid and vapours.

#### 8.2 Entering Tank/Vessel

- 8.2.1 A tank/vessel or any other confined space shall not be centered without a valid work permit clearing the equipment for safe entry.
- **8.2.2** Be sure that the equipment can be left by the original entrance. Put on a respiratory equipment and a relief rope.
- 8.2.3 One man on the outside of the tank should keep the man in the tank under constant observation, and at least two men should be available to aid in case of any risk to the man in the tank.
- **8.2.4** Special ventilation and a continuous fresh air supply are recommended during the entire time men are cleaning, inspecting or repairing the tank.
- 8.2.5 During the course of the work, tests shall be made to determine that no further washing is necessary, that no oxygen deficiency exists and that no harmful gas or vapour is present. This is essential as the residues which are not completely removed by washing get stirred up and may recontaminate the tank atmosphere.
- 8.2.6 On tanks having opening only at the top, complete removal of vapour has to be ensured. Chances of exhaust gases being recycled inside the tank should be eliminated.

#### 8.3 Repairs

- **8.3.1** No repair work such as cutting, riveting, welding should be undertaken on tanks and equipments unless a work permit has been issued by an authorised person.
- 8.3.2 In all cases, if repair work is interrupted for more than an hour, the work permit should be revalidated before resumption of work.

#### 9. PREVENTIVE MEASURES

#### 9.1 Personal Hygiene

- 9.1.1 As nitrobenzene is easily absorbed in human body, improve the equipment and operation methods lest nitrobenzene should leak or its vapour should transpire.
- **9.1.2** Adequate personal protective equipments are to be worn while washing, repairing tanks and other equipments or attending to leaks and spills.
- 9.1.3 The maximum concentration of nitrobenzene for a 60-minute exposure is considered to be 100 ppm. In case of a lower concentration for a short-time operation, a canister type gas mask may be used provided oxygen in the air is more than 16 percent by volume.

- 9.1.4 In case vapour concentration is unknown or is above 100 ppm or oxygen is less than 16 percent put on an air line respirator or self-contained breathing apparatus.
- 9.1.5 Carefully wash hands, face and feet before meal. A warm water bath before leaving the factory is essential, taking care to wash the head properly.
- 9.1.6 Avoid alcoholic drinks while being exposed to nitrobenzene or soon after the exposure, as these increase the risk of poisoning.
- 9.1.7 Do not chew, eat, drink or smoke with soiled hands or while working in nitrobenzene atmosphere.
- 9.1.8 It is advisable to absorb spillings in sand first and then wash the floor after collecting the moist sand to avoid exposure.
- 9.1.9 Work clothes should be compulsorily laundered every day on the premises. Clothing contaminated with nitrobenzene while working, shall be promptly removed and washed before re-use. To minimize the possibility of skin contact, men working with nitrobenzene should have two lockers and should be required to keep work clothing separated from personal clothing.
- 9.1.10 Emergency showers and eye wash fountains should be provided in areas where potential exposure to nitrobenzene exists.

#### 9.2 Personal Protection

- 9.2.1 Employee Education and Training
- 9.2.1.1 Safety in handling nitrobenzene depends upon the effectiveness of employee education, training and supervision.
- 9.2.1.2 The education and training of employees to work safely and to use personal protective equipment and other safeguards is the responsibility of supervision.
- 9.2.1.3 Workers should be thoroughly informed as to the hazards arising from improper handling of nitrobenzene. They should be cautioned to prevent spills and leakages and fully instructed regarding action to be taken in case of spills, splashes, vapour inhalation, and clothing contamination.
- 9.2.1.4 Workers should be specifically instructed that ingestion of even small amounts of alcoholic beverages preceding or following absorption of nitrobenzene will increase its toxic effects. Habitual users of alcohol shall not be permitted to work in the area where potential exposures to this compound exist.

9.2.1.5 Each employee should know what to do in an emergency and should realize the necessity for prompt application of first aid in case of contact with nitrobenzene or exposure to the vapour.

#### 9.2.2 Personal Protective Equipment

- 9.2.2.1 Personal protective equipment is not an adequate substitute for safe working conditions and intelligent conduct on the part of employees working with nitrobenzene. Though it is considered as a second line of defence, the proper and adequate usage of the protective equipment shall certainly reduce the severity of the incidences. Furthermore, in many instances, it is the only practical available means of protecting the worker in emergency situations.
- 9.2.2.2 The correct usage of the safety equipment requires proper education of the wearer in the use of the equipment available to him. Instruction and periodical drill regarding the location, purpose and use of personal protective equipment shall be ensured.
- 9.2.2.3 Employees who may be subjected to nitrobenzene exposures should be provided with proper protection for various parts of the body, as outlined below:
  - a) Long pants and shirts or overalls with long sleeves and head coverings. The shirt or overalls shall cover the neck completely.
  - b) Protective footwear made of washable material. If leather shoes are used, rubber overshoes shall be worn in areas wherever possibility of nitrobenzene contamination is likely to be present.
  - c) Suitable chemical safety goggles, gloves and apron shall be used, and
  - d) Where complete face protection is desirable, face shields may be used in addition to goggles.

Caution: Skin creams do not afford adequate protection.

- 9.2.2.4 Severe exposure to nitrobenzene vapour may occur in tanks, during equipment cleaning, repairs, during de-contamination following spills, failure of pipelines or equipments. Employees who may be subject to such exposures shall be provided with proper respiratory protection such as:
  - a) Air-line respirator,
  - b) Self-contained breathing apparatus, and
  - c) Canister type gas masks ( see 9.1.3 ).

Caution: Filter type respirators do not offer protection against gases and are unsuitable for use when working with nitrobenzene.

#### 10. DISPOSAL OF WASTE

- 10.1 Statutory regulations regarding health and pollution are to be strictly followed.
- 10.2 Waste may be washed away to a sewer after being diluted with a large quantity of water (approximately one percent slurry).
- 10.3 Care shall be taken to keep any person away from the place where waste materials are buried. It shall be made certain that there is no danger of pollution of underground water sources used as sources of drinking water.
- 10.4 Small quantities of nitrobenzene or waste may be disposed off by burning.

#### 11. MEDICAL MANAGEMENT AND FIRST AID

#### 11.1 General

11.1.1 Health Examination at the Time of Employment—As a worker who handles nitrobenzene, it is unsuitable to employ an anaemic person, a person with heart and kidney trouble, a person suffering from any urinary disease, a person prone to allergy, and a heavy drinker. Carry out a blood test and employ a normal healthy person.

#### 11.1.2 Regular Health Examination

- 11.1.2.1 Regular health examination shall be carried out at intervals of not more than 3 months.
- 11.1.2.2 Conduct blood tests every month. It is necessary to check the conditions of workers who may be exposed to nitrobenzene from time to time and confirm that no case of anaemia is found.
- 11.1.2.3 By conducting urine tests (urobilinogen, propyrin, occultblood test, and the deposit), acute and chronic poisoning of nitrobenzene may be prevented. It is desirable to carry out the examination of urine once in two weeks, especially once a week in summer.

#### 11.2 Suggestions to Physicians

11.2.1 If possible, while the patient is accutely ill, methemoglobin concentrations of the blood should be determined quantitatively at least every half an hour. Such check should be continued until it is established definitely that the concentration of methemoglobin is steadily decreasing.

- 11.2.2 If the concentration of methemoglobin reaches 40 percent in venous blood samples, 1000 ml of 5 percent glucose may be administered intravenously and repeated in an hour, if necessary. This appears to stimulate the reversion of methemoglobin to hemoglobin.
- 11.2.3 The patient shall be comfortable in an oxygen tent. Oxygen serves to relieve headache transiently, apparently due to supersaturation of the hemoglobin and plasma with oxygen, but does not seem to hasten the reversion of methemoglobin to hemoglobin. Under such treatment, acutely toxic patients with methemoglobin concentrations as high as 76 percent in venous blood samples usually make eventful recoveries within 24 hours, with no demonstrable permanent, residual pathology.
- 11.2.4 It is imperative that patients be closely observed and remain in bed for 24 hours if methemoglobin content has reached 40 percent.
- 11.2.5 An intravenous injection of 10 to 20 ml of 2 percent ammonium thiosulphate and a large dose of vitamin C at one time shall contribute to a quick recovery.

#### 11.3 First Aid

#### 11.3.1 General

- 11.3.1.1 Take off the contaminated clothes at once and wash the skin immediately and thoroughly with plenty of soap and tepid water. Speed in removing nitrobenzene from the skin is of prime importance.
- 11.3.1.2 Do not put on contaminated clothes again unless they are cleaned up sufficiently.
- 11.3.1.3 Carry a toxic patient on a stretcher to the medical department or first aid station.
- 11.3.1.4 No matter how slight his symptoms are, refrain from speaking loudly or doing anything which may disturb the patient.
- 11.3.1.5 Do not give a patient any such stimulant which contains alcohol. Do not use any tincture (containing alcohol) as a cardiac.
- 11.3.1.6 If a patient has consciousness, he may drink fluids containing carbohydrates, such as, orange juice and sweetened lemonade.
- 11.3.1.7 Even though severe headache is complained of, drugs such as acetanilide, acetophenetidine and other methemoglobin producers shall not be given. Headache may be relieved by codeine administered by nursing personnel.
- 11.3.2 Contact with Skin Remove all contaminated clothing. Get under an emergency shower. Wash the affected areas thoroughly with soap and tepid water.

- 11.3.3 Contact with Eyes Wash the eyes with a large amount of water, holding apart the eyelids, for at least 15 minutes. Though nitrobenzene does not give too much irritation to the eyes, it is apt to injure the cornea. A competent physician should be consulted as early as possible.
- 11.3.4 Ingestion Ingestion of nitrobenzene should be treated by the administration of an emetic such as mustard and water or a lukewarm emulsion of soap and water, provided the patient is conscious.

Caution: Never give anything by mouth to an unconscious person.

11.3.5 Inhalation — Inhalation of the vapour requires the same treatment as that for skin absorption or ingestion except that an emetic is needed only when nitrobenzene is swallowed.

(Continued from base 2)

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